APR 2005

ff0/532200

Recyclable crosslinked polymers with saturated main chain and thermally reversible urethane crosslink points

Technical field

The invention relates to saturated backbone polymers of improved heat resistance above their glass transition temperature (in the case of amorphous polymers) and/or above the melting point of their crystalline phase (in the case of semicrystalline polymers), which can be recycled at an elevated temperature by conventional melt processing methods, wherein the heat stability is provided by thermally reversible urethane bonds as crosslink sites dissociating at a temperature above the glass or melting range but below the onset of the thermal degradation of the polymer.

Background of the invention

Normally the thermal resistance of thermoplastic materials is limited by their softening, which (in the case of amorphous polymers) occurs above the glass transition temperature (T_g) where the mobility of the macromolecules or their large segments increases abruptly. Below that temperature the material behaves as a rigid glass, above the glass transition temperature the material softens gradually (it becomes a viscoelastic "rubbery" material) and at even higher temperatures it becomes a viscous melt. The width of the "rubbery plateau" depends on the average molecular mass. The usefulness of glassy polymers is limited, however, by their rigidity and brittleness. Other materials, as e.g. saturated polyolefins (polyethylene, isotactic and syndiotactic polypropylene, polyisobutylene etc.) exhibit two characteristic transitions: the glass transition (T_g) and the melting point (T_m) of the crystalline phase (the latter is always higher than the former, usually T_g = 0.6-0.8 *T_m). These molecules exhibit enough symmetry and flexibility to develop micro-crystals but a fully crystalline sate cannot develop due to mobility restrictions. These materials exhibit an interesting "leathery" structure between the two transition temperatures, where tiny crystalline particles are connected by less

organized ("amorphous") polymer chains of increased mobility. These semicrystalline materials exhibit superior mechanical properties to pure amorphous polymers as the crystallites act a "physical crosslinks", so the deformation is limited (provided that the stress is not high enough to destroy the crystallites as e.g. in the case of "stress

5 whitening"). If, however, the temperature approaches the melting point of the crystalline phase (which is broadened, due to the crystallite size distribution) the mobility increases and the mechanical properties (modulus and strength) degrade abruptly (usually even more abruptly than in the case of the glass-rubber transition, where the change is more gradual).

10

There are certain applications, however, where the products made of semicrystalline materials spend most of their time at temperatures between the glass transition and the melting temperatures but occasionally thermal overloads may happen and in these cases it is required that the material should not melt and flow, but exhibit a certain degree of

15 mechanical resistance. Two typical examples are cable insulation materials (under overloading conditions) and water pipes used in floor heating. This problem can be partially solved by chemical (or radiation) crosslinking of the material (see e.g. K. Kircher: Chemical Reactions in Plastics Processing, Hanser Publishers, Munich, 1987), which may influence the degree of crystallinity, but does not eliminate it (see e.g. I.

20 Chodak: Properties of Crosslinked Polyolefin-Based Materials, Prog. Polym. Sci., 20, 1165-1199 (1995)). Crosslinked semicrystalline materials exhibit a soft rubber-like behavior between the melting point of the crystalline phase and the thermal degradation temperature of the network. The mechanical properties in this temperature range are much inferior to those exhibited between the melting point and the glass transition

25 temperature, but they are sufficient to prevent material flow and even a certain degree of strength remains. The presence of crosslink sites (network formation), however, seriously limits the recycling possibilities of products made of such materials.

Crosslinked polymers can be re-processed only by milling/grinding (sometimes at

30 cryogenic temperature) or by thermo-mechanical degradation (random scission) at elevated temperature (see e.g. JP 11189670). The former method produces organic fillers of limited value at a relatively high price, the latter yields a melt with strongly

branched molecules and broad molecular mass distribution, which cannot be processed by itself, only in combination with virgin thermoplastics (see e.g. JP 10230520). The thermo-mechanical degradation at high temperature (see e.g. JP 11100448) involves large energy consumption (thermal and shear degradation) and leads to high defect concentration in the reprocessed material. Thus it is desirable to develop materials, which exhibit improved properties above the melting point of the crystalline phase but can be re-processed by conventional melt technologies.

State of the art

One obvious way of eliminating the drawbacks of permanent crosslinking is to build up (thermally) reversible crosslinks. A relatively early review of this method (R.W. Rees: Cross-linking, reversible, in: Encyclopaedia of Polymer Science and Engineering, ed. H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, Wiley Interscience, New York (1986), pp. 395-416) lists the following possibilities:

- ionomer formation
- amine-salts
- reversible Diels-Alder reaction (cyclopentadienes, opening with maleic anhydride)
- dimerisation of nitroso groups
- reversible esterification
- anhydride crosslinking
- complex formation
- disulfide bridges.

All these crosslink sites undergo more or less reversible dissociation under the effect of heat, or, in some cases, in the presence of certain chemicals (see e.g. US 6,090,862).

Several patent applications have been submitted which are based on reversible esterification reaction between cyclic anhydrides and polyols (e.g. JP 11181200 or

US3678016 for styrene based resins, JP 11106578 or JP 07094029 for polyolefin based resins).

JP 10338711 describes a thermally reversible crosslinked system using a hindered amino group-containing compound – combined with acids. All examples of the patent come from acrylic resins.

US5654368 provides elastomer-like or rubber-like, recyclable cross-linked polymers capable of being liquefied and re-molded repeatedly without detracting from the physical properties of the polymers. The polymer comprises meltable cross-linked oligomer units and linkage units through which the oligomer units are linked to construct the main chains of the polymer. The reversible crosslink sites are based on disulfide bonds, which can be disrupted and regenerated in redox reactions. Other crosslink-sites mentioned in the patent include ester bonds, furane-maleic anhydride Diels-Alder adducts, Si-Si bonds, photo-dimerized coumarin and anthracene ring units.

US4882399 describes an epoxy system with thermally reversible crosslinks. It contains disulfide bridges, which can be cleaved in proper solvents and regenerated under mild oxidizing conditions.

US3890253 describes reversible cross-linking imparted to polymers and copolymers, especially of the vinyl, olefinic, and olefinic oxide types by means of recurring dicyclopentadiene linkages. Difunctional dicyclopentadiene compounds can be polymerized directly into homopolymers or polymerized with comonomers to form copolymers. Alternatively, polymers carrying cyclopentadiene substituents can be prepared and the dimerization of the cyclopentadiene groups effected *in situ* to produce the cross-linkages. The dicyclopentadiene crosslinkages cleave on heating to a sufficient temperature so that the present polymers and copolymers have a thermoplastic character notwithstanding their normal crosslinked network structure.

DE 10046024 describes a wide range of *elastomers* with thermally reversible crosslink points based (among others) on the following linkages:

-   acid anhydride group and an alcohol group

-   carboxyl group and a vinlyether group

-   alkyl halogenide group and a tertiary amine group

-   isocyanate group and a phenolic group

5   -   azlacton group and a phenolic group

-   dimerised nitroso groups

-   interaction between N-containing heterocycles.

The patent defines the *elastomer* as a polymer, which has a T_g below 25 °C (preferably

10   below 10 °C). It can be any natural or synthetic polymer, which has rubber-elastic
properties and which can be vulcanised by proper chemicals into a rubbery network.
They may include natural rubbers, thermoplastic elastomers or even saturated
polyolefins as polyisobutylene, ethylene-propylene-diene rubber or even chloro-
sulfonated polyethylene. Most of these polymers contain residual double bonds

15   (unsaturations) to make possible standard vulcanisation by sulphur. According to he
patent the functional groups forming the crosslink site can be both located on polymeric
components, or one of them can be attached to the polymer, the other can be a low
molecular compound, acting as a crosslinker. The patent does not restrict the way of
attaching the functional groups to the polymer chains, it can be done by

20   copolymerisation, grafting etc., although in the examples direct addition reactions (as
e.g. in the case of maleic anhydride) or addition reactions via mercapto-functionalised
monomers (as e.g. mecapto-phenol) to the residual unsaturations are mentioned. Both
solution-based and "dry" methods, such as kneading are allowed to perform the
reactions, although most examples mention solvent-based methods. In the example of

25   isocyanate + phenol bond e.g. the isoprene rubber is first reacted in xylene solution with
mercapto-phenol, then it is precipitated, dried and mixed with diphenylmethane-
diisocyanate (MDI) in a kneader. The content of the crosslink-forming functional
groups is preferably below 0.1 mol%. Typically the rubbers with thermo-reversible
crosslinks begin to flow at 150-170 °C, which makes possible melt-recycling.

30

The thermal reversibility of urethane bonds formed by the reaction of isocyanates and
alcohols is also well known and utilised both in the recycling of polyurethanes and

especially in developing blocked iscoyanates which react only under the effect of heat, in the presence of properly chosen catalysts (see e.g. Polyurethane Handbook, Ed.: G. Oertel, Hanser Publishers, Munich 1985, pp., 8, 10, 15, 78, 84, 522, 533, 540). The typical "reversion" temperatures for various kinds of urethane bonds are as follows (see

5   the reference quoted above, p. 84):

n-alkyl-NH-COO-n-alkyl   ~250 °C
aryl-NH-COO-n-alkyl   ~200 °C
n-alkyl-NH-COO-aryl   ~180 °C
10 aryl-NH-COO-aryl   ~120 °C

Phenol blocked icoyanates have been widely used, but later more advanced blocking agents (such as oximes, caprolactam, maleic acid esters, acetyl-acetone derivatives or other CH-acids) were developed to prevent the formation of toxic phenolic compounds
15 during the de-blocking reaction, or macromolecular phenols (such as coumarone-indene resins etc.) were used, which do not produce volatile reaction products on deblocking. The deblocking reaction of blocked isocyanates is performed in the presence of a large amount of alcohol groups, and is catalysed by catalysts commonly known to catalyse trans-esterification and/or urethane formation. These include teritary amines, Lewis-
20 acids (especially tin compounds, such as tin-(II) salts of carboxylic acids, dialkyl tin salts of carboxylic acids, Bi, Pb, Zn, Zr salts of medium and long chain fatty acids, various metal-acetylacetonates see e.g. Polyurethane Handbook, Ed.: G. Oertel, Hanser Publishers, Munich 1985 and K. Kircher: Chemical Reactions in Plastics Processing, Hanser Publishers, Munich, 1987).
25

WO0192366 describes a polyurethane system with thermally reversible bonds, based on urethane groups formed between isocyanates and benzylic OH groups.

Thus, from the above elements it seems possible to develop polyolefins and other
30 thermoplastic polymers of saturated molecular main chain by introducing thermally reversible urethane linkages. Taking into account the approximate decomposition temperatures quoted above, the combination of aromatic isocyanates and phenols seems

to be optimal for reversible crosslinks to be processed by melt methods if the matrix is polyethylene (melting point 110-135 °C) and a combination of aliphatic isocyanates and phenols for polypropylene based matrices (melting point above 150 °C), although the actual reversion temperatures depend on other factors, as medium polarity, presence and

5   type of catalysts etc. These polymers would exhibit improved heat resistance above the glass transition temperature or above the melting point of the crystalline phase, but could be re-processed by conventional melt-technologies at a temperature above the thermal dissociation temperature of the urethane bond but below the thermal decomposition of the bonds constituting the main chain. Nevertheless there are several

10   problems, which have to be solved, and which are not described in the patents published so far.

These problems are as follows:

15   -   the reversible reaction of phenolic and isocyanate groups is to be realised in a dilute, non-polar environment

      -    mobile reagents of medium or high polarity (compounds with phenolic and/or isocyanate groups) should be distributed in a non-polar, high viscosity medium (in melt, as solutions methods should be avoided due to their complexity, higher

20   price and environmental problems) and phase separation during the reaction should be avoided

      -    the phenolic and/or isocyanate functional groups should be attached to the saturated main chain by radical grafting (there are no residual double bonds to allow for thiol addition, as in the case of typical elastomers) without creating

25   thermally irreversible C-C crosslink sites. This requires the judicious choice of peroxide (or other radical source) and the proper selection of the concentration and reactivity of the compounds to be grafted.

      -    a proper catalyst package should be found which is compatible with the non-polar matrix, which is not volatile and which allows for repeated re-formation of

30   urethane linkages after thermal dissociation

-       the catalyst package and the phenolic components should be possibly selected so
        as to reduce the number of necessary additive components (it can be achieved by
        using multi-functional additives).

5   It is our objective to solve these non-trivial problems and to provide formulations with
       the above properties as well as processes for their manufacture. The main intended area
       of application is cable insulation and/or sheathing produced by continuous vulcanisation
       (CV) methods or cable insulation in oil-filled (OC) cables.

10   **Detailed description of the invention**

       In one aspect the invention provides thermoplastic polymer compounds with thermally
       reversible urethane linkages comprising
       a.) a thermoplastic polymer component (homopolymer, copolymer or polymer mixture)
15   with saturated molecular main chain
       b.) an isocyanate group either attached to the polymer chain (by copolymerisation,
       grafting or by polymer-analog reactions) or being present in mobile form in the polymer
       matrix
       c.) a phenolic (optionally aliphatic, or cycloaliphatic) hydroxyl group either attached to
20   the polymer chain (by copolymerisation, grafting or by polymer-analog reactions) or
       being present in mobile form in the polymer matrix
       d.) a catalyst package which promotes the reversible formation and thermal dissociation
       of urethane bonds
       e.) optionally a processing aid to facilitate the homogeneous distribution of polar active
25   components and/or catalysts in the compound,
       wherein, if the isocyanate group is attached to the main chain, the hydroxyl component
       exhibits an average functionality of at least 2; if the hydroxyl component is attached to
       the main chain, the isocyanate component exhibits an average functionality of at least 2,
       or if both components are attached to the main chain, the functionalized polymer
30   molecules themselves exhibit an average functionality of at least 2, and the urethane
       bonds formed by the reaction of the isocyanate and hydroxyl groups undergo reversible
       thermal dissociation at a temperature between the glass transition temperature or

melting point of the thermoplastic polymer and the thermal degradation temperature of the thermoplastic polymer.

The polymer matrices used in the invention are saturated backbone vinyl polymers and copolymers (such as ethylene-vinyl acetete /EVA/, etyhlene-acrylic acid /EAA/, ethylene- ethyl acrylatre /EEA/ etc.), preferably polyolefins. Polyolefins include all kinds of polyethylenes (high density, low density, linear, metallocene etc.), polypropylenes and their copolymers (random or block) and blends (including dynamically vulcanized thermoplastic elastomers). Our main concern is to improve the heat resistance of low density polyethylene (LDPE), which is widely used for medium and high voltage cable insulation, where the continuous use temperature is 90 °C, but occasionally it can rise to 110 °C or higher (short circuit conditions). This temperature resistance so far could be achieved only by XLPE (crosslinked polyethylene) or by EPDM (ethylene-propylene-diene monomer copolymer) insulations – neither can be recycled by conventional methods. The use of higher melting point HDPE (high density polyethylene) or PP (polypropylene) or PE-PP copolymers instead of LDPE has been prevented by the inferior mechanical (rigidity) or electrical (breakdown) properties of these alternative materials, although recent patents (see e.g. WO0041187) indicate the viability of this route. LDPE grades with thermally reversible crosslink points could be utilized, however, not only in cable insulation, but in several other areas, as heat resistant water tubes, packaging, heat shrinking materials etc.
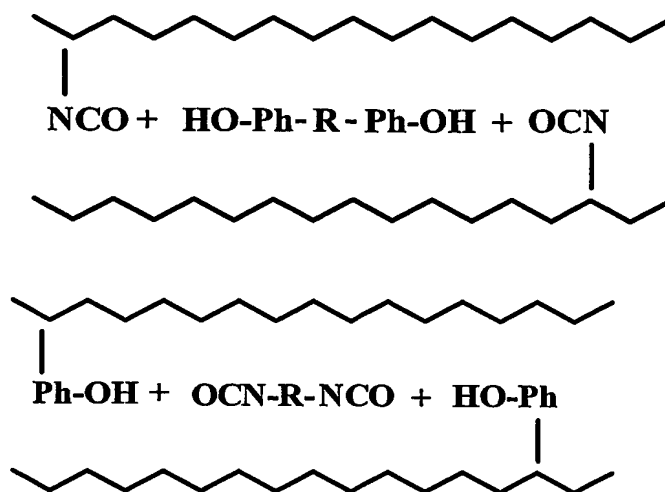
Formally there are at least three different ways of preparing the reversible urethane
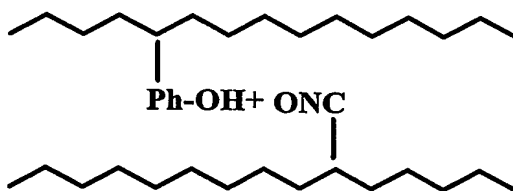
linkages:

a) Coupling both the hydroxyl and isocyanate components to the main chain of the polymer

b) Coupling the isocyanate component to the polymer, and adding the polyol component in mobile (but not volatile) form

NCO + HO-Ph-R-Ph-OH + OCN

Ph-OH + OCN-R-NCO + HO-Ph

5   c) Coupling the hydroxyl component to the polymer, and adding the polyisocyanate in mobile (but not volatile) form.

In principle the hydroxyl and/or isocyanate groups can be incorporated into the main chain by copolymerisation (an this possibility is not excluded from the invention) but

10   the preferred way of coupling the reactive groups to the main chain is via radical induced grafting, as this does not require a separate synthetic step and allows the utilisation of existing, commercially available polymer grades. (If the main chain is polypropylene or an etyhlene-propylene copolymer care must be taken to avoid excessive chain scission, which may occur in the presence of peroxides).

15

The isocyanate component may be grafted to the main chain through a double bond. It can be done by any monomer containing at least one isocyante group and at least one olefinic double bond, e.g. isocyanto-ethyl-acrylate or -methacrylate or isoyanato-propyl-acrylate or methacrylate. If the isocyanate group is grafted onto the main chain, the

20   mobile hydroxyl component can be any polyphenol of low volatility, as e.g. dihydroxy and tirhydroxy benzenes, or any oliogomer or polymer containing phenol groups (novolak resins, other phenol-formaldehyde resins, cumarone-indene resins etc.). The polyphenol can also be a polyvalent phenolic antioxidant or thermal stabilizer commonly used in olefinic resins (such as e.g. Irganox 1010, Santonox R etc.). In this

case, however, less strongly hindered phenols should be selected and the formation of urethane bonds should be checked individually. The hindrance of the phenol group may also influence the thermal dissociation temperature of the urethane bond formed and this effect could be utilised to "fine tune" the decomposition temperature of the urethane

5 link. If antioxidants are utilised to form urethane bonds, the reduced concentration of the antioxidant groups should be taken into account when designing the stabiliser package. This approach decreases the number of necessary additive components by using a multi-functional additive.

10 It is also possible to attach aliphatic alcohol groups to the main chain of the thermoplastic polymer and to react it with a prepolymer containing diisocyanates and polyphenols with a functionality of 2 or higher. In this case the urethane bonds formed in the aliphatic alcohol – isocyanate reaction will dissociate at higher temperature than those formed in the isocyanate – phenol reaction. An example for this last system is to

15 graft hydroxy-ethyl methacrylate to the main chain of the thermoplastic polymer and to react it with an MDI-phloroglucinol prepolymer.

If the (phenolic) hydroxyl component is grafted to the main chain, any phenol containing an olefinic side group may be used, as e.g. allyl-phenol, hydorxy-styrene,

20 vinyl-hydroxy napthalene etc. It is also well known that certain phenolic antioxidants belonging e.g. to the thio-bisphenol class (e.g. Santonox R) can be easily grafted to the polyethylene main chain in the presence of radical initiators (presumably through the broken sulfur bonds). As Santonox R is widely used as antioxidant in cable insulation, its use as a graftable phenolic component (multi-functional additive) again reduces the

25 number of necessary additive components. The reduction of active phenol concentration (by urethane formation) in the antioxidant activity should be take into account, however. Once the phenolic group is attached to the main chain, the crosslinking can be achieved by any di- or polyisocyante monomer or prepolymer commonly used in the polyurethane industry, e.g. toluylene-diisocyanate (TDI), methylene-diphenyl –

30 diisocyanate (MDI), and their dimers, trimers, prepolymers etc. (for a more complete list see: Polyurethane Handbook, Ed.: G. Oertel, Hanser Publishers, Munich 1985 and

K. Kircher: Chemical Reactions in Plastics Processing, Hanser Publishers, Munich, 1987). Preferably aromatic diisocyanates with low vapour pressure are used.

Of course both phenolic and isocyanate groups may be grafted onto the main chains using the unsaturated isocyanate or phenol containing molecules mentioned above.

5

For the realisation of the invention proper reaction partners, (urethane) catalysts, reaction conditions (for grafting, urethane formation and reversion) and processing technologies must be found.

10   The urethane catalyst package has to be effective, heat stable, non-volatile, compatible with the polymer, and should not affect the final properties of the polymer (e.g. the insulation properties of a cable insulation). It is advisable to use catalysts, which are used not only in polyurethane chemistry, but are also known and proven additives in thermoplastic polymers, as polyolefins. Commonly used urethane catalysts include

15   teritary amines, Lewis-acids (especially tin compounds, such as tin-(II) salts of carboxylic acids, dialkyl tin salts of carboxylic acids, Bi, Pb, Zn, Zr salts of medium and long chain fatty acids, various metal acetyl-acetonates see e.g. Polyurethane Handbook, Ed.: G. Oertel, Hanser Publishers, Munich 1985 and K. Kircher: Chemical Reactions in Plastics Processing, Hanser Publishers, Munich, 1987). Usually a combination of metal

20   salts and tertiary amines is used. One interesting possibility, which is a part of the present invention, is to utilise hindered amine stabilisers (commonly known as HALS stabilisers) as amine catalysts, as the can also play the role of antioxidants and/or voltage stabilisers (radical scavengers) in high voltage cable insulation - thus the number of additives can be reduced by using a multi-functional additive. It is

25   advantageous to use metal salts of long chain fatty acids as co-catalysts, as these compounds are widely applied as lubricants in polyolefins (again a multi-functional additive). It is especially advantageous to use HALS (hindered amine light stabiliser) – Zn-stearate as a catalyst-co-catalyst system.

30   The grafting conditions should be selected so that the main chain radical (R·) concentration is low enough to avoid recombination (R-R) and the reactivity of the isocyanate and/or hydroxyl group containing molecule should be high enough with the

main chain radicals. This can be achieved by the proper selection of the radical generating species (usually peroxide, azo-bis-isobutyro-nitrile, AIBN or other radical initiator) and the reaction temperature. Interactions between the radical generating species and the hydroxyl component to be grafted or the phenolic antioxidants and thermal stabilizers present in the polyolefin matrix should be taken into account to avoid the degradation of stabiliziers.

In another aspect the invention provides a process to prepare the compounds described above consisting of the following steps:

a) preparing a first additive package containing the monomer(s) (which can be the isocyanate component or the hydroxyl component) to be grafted and the radical source (e.g. peroxide) and the (optional) processing aid, by mixing the processing aid first with the radical source, then with other component(s)

b) preparing a second additive package containing the other urethane forming component (if the hydroxyl component is present in the first package, then the isocyanate component, if the isocyanate component is present in the first package, then the hydroxyl component), the processing aid, the urethane catalysts and, if both the hydroxyl and the isocyanate components are grafted, the radical source (e.g. peroxide), by mixing first the processing aid with the solid components, then with other component(s)

c) melting the thermoplastic polymer

d) mixing the first additive package with the molten polymer at a temperature where the grafting reaction is complete within a few minutes

e) mixing the second additive package with the molten polymer at a temperature where the urethane formation reaction, and, if necessary the grafting, is complete within a few minutes

f) after proper shaping (e.g. extrusion/granulation, injection, etc.) the compound is cooled down.

So far the problems of distributing the components in the polymer matrix and the formation of urethane bonds have not been discussed. It is well known that low molecular additives with a polarity different from that of the matrix tend to phase-

separate and accumulate at crystal boundaries or in the amorphous phase of polyolefins, which may lead to problems (uneven crosslink distribution, formation of breakdown sites in high voltage insulation, weak spots in oxidative or hydrothermal degradation environment etc.). It is also advisable to graft and distribute the hydroxyl and isocyanate

5   components separately to avoid the agglomeration of urethane groups. These problems can be conveniently solved by adding the components in the form of separate additive packages, which is an important feature of the present invention. If only one of the components are grafted (e.g. the hydroxyl or the isocyanate component), then the grafted component should be combined with the radical source as the first package, and

10   the other component should be combined with the urethane formation catalysts as the second additive package and should be distributed in the polymer subsequently. If both urethane components are grafted the second package should also contain a radical source. If multi-functional additives - either the phenol stabilizer (which may be utilized as a crosslinking agent) or the HALS stabilizer (which may be utilized as an urethane

15   co-catalyst) - are already present in the polyolefin compound to be modified, the preparation of additive package may become simpler.

When distributing minor amounts of low molecular or oligomeric additives in a polymer melt homogeneously, it may be useful to use processing aids, such as high

20   surface area or porous mineral additives, which may absorb the additives in the preparation phase of the additive package and may release them in the processing phase. (This also reduces the probability of explosion if peroxides are used as radical intiators). Examples for such materials include zeolites or other micro-porous silicates and various lamellar silicates, as montmorillonite, bentonite, clay, talc or mica. In order to enhance

25   the compatibility of such minerals with the organic additives they may be rendered organophilic by various surface treatments, such as silane modification etc. It is especially   advantageous   to   use   commercially   available   organophilic bentonites/montmorillonites (e.g. those mentioned in the Examples). If the additives and the processing conditions are properly selected, a partial or complete exfoliation of

30   these organophilic clays may even increase considerably the mechanical, flammability, thermal etc. properties of the matrix resin (nano-composite formation). If one or more components of the additive packages are liquid, pastes can be prepared and

conveniently added to the polymer. If none of the components are liquid, solvents may be used to promote the absorption of the components by the processing aid and later this solvent can be removed by distillation or drying.

5   Preparation of the compounds may be realized in various melt-mixing devices, such as kneaders, mixers, compounding extruders, Buss co-kneader etc., followed by direct shaping or by granulation. It is especially advantageous to utilize multi-port compounding extruders with multiple entries for solid/liquid/paste additives. In this case the separate addition and grafting of various components can be realized in a continuous

10   technology. The granulated product can be later processed by any convenient melt processing technology as compression moulding, injection moulding, extrusion, film blowing etc.

The invention is illustrated by the examples listed below, but they do not limit the scope

15   of the invention. Several alternative possibilities are obvious for those skilled in the art, which are still within the scope and spirit of the invention, limited only by the claims.

FIGURES

20   Fig. 1. Arrhenius plot of the viscosity of a paraffin sample crosslinked by 2 phr Perox TB in the presence of TAIC (2 mol TAIC for 3 mol Perox TB). For abbreviations see Table 5.

Fig. 2. Arrhenius plot of the viscosity of a paraffin sample grafted by 0.5 phr Perox TB-

25   HEMA (2 Mol HEMA for1 Mol Perox TB) and crosslinked by TDI-PHL adduct on heating and cooling. For further details see Tables 5 and 6.

Fig. 3. Arrhenius plot of the viscosity of a paraffin sample grafted by 1.0 phr Perox TB-HEMA (2 Mol HEMA for1 Mol Perox TB) and crosslinked by TDI-PHL adduct on

30   heating and cooling. For further details see Tables 5 and 6.

Fig. 4. Micro-thermal analysis curves of a non-crosslinked PE sample (sample No. 02-33) and three samples with thermally reversible crosslinks, prepared according to Examples 3, 4 and 5 (for sample notation see Table 8.).

5   Fig. 5. Micro-thermal analysis curves of a non-crosslinked PE sample (sample No. 02-33) and three samples with thermally reversible crosslinks, prepared according to Examples 6, 7 and 8 (for sample notation see Table 11.).

Fig. 6. Micro-thermal analysis curves of a non-crosslinked PE sample (sample No. 02-10   33) and three samples with thermally reversible crosslinks, prepared according to Examples 9, 10 and 11 (for sample notation see Table 13.).

Best mode to carry out the invention

15   The reactions used to optimize the polyurethane catalysts (see examples 1. and 2.) were evaluated visually.

The viscosity of the grafted/crosslinked paraffin mixtures used to optimize the reaction conditions and to prove the reversibility of urethane crosslink formation was determined 20   by a standard falling ball viscometer of the Höppler type, where the temperature is regulated by a circulating bath.

Melt processing experiments (examples 3-11) were performed in a Brabender Plastograph PL 2000 type equipped with an internal mixer chamber (useful volume is 25   250 cm^3). The same equipment was utilized to monitor the re-processability of the crosslinked mixtures.

For detecting the breakdown of the crosslink points in the melt-processed samples the method of Micro-Thermal Analysis (μTA) was also used (TA Instruments, Inc.). This 30   method measures the thermal response, providing information similar to that obtained from conventional thermal analysis. The thermal probe is made from a tiny platinum filament surrounded by a silver sheath. The wire is formed into a probe and the silver is

etched away to reveal the platinum tip. A laser beam is reflected by a mirror from the probe to a photodetector. Changes in probe position will generate a change in photodetector voltage. µTA also images the thermal conductivity and thermal diffusivity near to the surface. The probe acts as a resistive heater and provides the

5   means of measuring the temperature. The temperature program applied to the probe can be modulated. In the LTA (localized thermal analysis) experiments the probe heats the sample, and thermal expansion or softening effects can be monitored by detecting the movement of the laser signal on the photodetector. This measurement can be used to determine expansion, softening, melting or glass transition. Changes in the thermal

10   conductivity and thermal diffusivity of the near-surface region also can be measure when the probe is heating. For detection the presence of crosslinks and the thermal dissociation of crosslink the LTA analysis function was applied. A 0.5x5x5 mm size freshly cut flake of the compound was glued onto the table of the device. The thermal probe was heated at a rate of 10°C/s in the temperature range of 30-200°C after placing

15   the probe on the surface of the sample with a 56 nN loading.

Example 1.

20   *Selection of polyurethane catalysts and the proof of reversible reaction*

For the selection of urethane catalysts and to prove the reversibility of the urethane reaction solution conditions were used, which can be investigated and screened easier than melt-reactions. As a solvent Diphyl (a commercially available heat-transfer

25   medium, a mixture of diphenyl oxide and diphenyl) was used (melting point 12.2 °C, boiling point 265 °C), as it has low volatility, dissolves the components and allows reaction kinetic studies in a wide temperature range. For the reaction-kinetic studies TDI (toluylene-diisocyanate) was selected as iocyanate component and thymol as a phenolic component (see Table 1.).

30

Table 1. Properties of the isocyanate and phenol components used in selecting the urethane catalysts.

Compound	Formula	Mw.	Mp. (°C)	Bp. (°C).	Weight loss (TG) °C	%
Toluylene-diisocyanate (TDI) Aldrich (USA)	$C_6H_4(NCO)_2$	160	12-14	251	80 125 148 173	0 5 10 20
Thymol (THYM) (Reanal Fine Chemicals Co. Hungary)	$(CH_3)(C_3H_7)C_6H_3OH$	150	51	232	115 140 150 160 170	0 5 10 15 25

The catalysts screened are listed below in Table 2.:

Compound	Appearance, use
Amine catalysts	
Pyridine (PYR) (Reanal Fine Chemical Co. Hungary)	Liquid
Chimassorb 944 (ChS944) (CIBA-GEIGY)	Powder Polymer HALS type stabiliser
Chimassorb 119 (ChS119) (CIBA-GEIGY)	Fine granules Polymer HALS type stabiliser
Metal salt catalysts	
Dibutyl tin dilaurate (DBSnDL)	Solution Trans-esterification catalyst
Mg-naphtenate (MgNaph) . *BUDALAKK-TITÁN Festékgyártó Kft.*, Szeged, Hungary	Paste Catalyst for coatings
Mn-octoate (MnOct) . *BUDALAKK-TITÁN Festékgyártó Kft.*, Szeged, Hungary	Paste Catalyst for coatings
Zn-octoate (ZnOct) . *BUDALAKK-TITÁN Festékgyártó Kft.*, Szeged, Hungary	Liquid thick viscous Catalyst for coatings,
Zn-stearate (ZnSt)	Powder

SUBSTITUTE SHEET (RULE 26)

FACI	Lubricant for thermoplastics

As one can see, in both categories, we tried to use not only traditional urethane catalysts but also other additives known in thermoplastics (e.g. HALS stabilizers or metal soap lubricants), which are expected to be both effective catalysts and known to be compatible with polyolefin matrices.

The components (relative amounts in weight parts given in Table 3.) were weighed into a stoppered test tube. After intense homogenization of the components, the test tube was capped with a CaCl$_2$ tube, and immersed in an oil bath of 100°C, until a reaction took place, but maximum. for 60 minutes. The reaction mixture was cooled back to room temperature. Finally the samples were heated again, but this time to 135 °C and kept there for 15 min. The changes in color, viscosity and phase transitions during heating and cooling were observed (see Table 3.).

Table 3. Compositions of samples with one kind of catalyst and observations

Components	Code of compounds Proportion of components (in weight parts)					
sample No.	F/01/0	F01/1	F/01/2	F/01/3	F/01/4	F/01/5
TDI	1.3	1.3	1.3	1.3	1.3	1.3
THYM	2.4	2.4	2.4	2.4	2.4	2.4
DIPh	2.9	2.9	2.9	2.9	2.9	2.9
PYR	0.08					

Components	Code of compounds Proportion of components (in weight parts)					
ChS944		0.08				
DBSnDL			0.08			
ZnSt				0.08		
ZnOct					0.08	
MgNaph						0.08
Evaluation based on observations						
At room temp. after preparation	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid
At 100 °C after heating	Thin, viscous after 60 min.	Thin, viscous after 60 min.	Solid after 5 min.	Solid after 52 min.	Solid after 41 min.	Solid after 29 min.
At room temp. after cooling	Thin liquid	Thin liquid	Solid	Solid	Solid	Solid
At 135 °C after heating	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid
At room temp. after cooling	Thin liquid	Thin liquid	Solid	Solid	Solid	Solid

Abbreviations: (for other abbreviations see Tables 1. and 2.)

DIPh = diphyl

5   The data in the Table 3. prove: a.) the reversibility of urethane formation and b.) that the catalysts (with the exception of dibutyl-Sn(II)-dilaurate) are not effective enough to

promote the formation of urethane bonds at 100 °C within a few minutes (typical processing time for polyolefins). Therefore, in a next experiment (see Table 4.) amine type catalysts were combined with metal-based catalysts to see the effect of co-catalysis on the urethane formation.

5   Table 4. Compositions of samples with combined catalysts and observations

Components	Code of compounds Proportion of components						
sample No.	F/01/6	F/01/7	F/01/8	F/01/9	F/01/10	F/01/11	F/01/12
TDI	1.3	1.3	1.3	1.3	1.3	1.3	1.3
THYM	2.4	2.4	2.4	2.4	2.4	2.4	2.4
DIPh	2.9	2.9	2.9	2.9	2.9	2.9	2.9
PYR	0.08	0.08	0.08		0.08		
ChS944				0.08		0.08	
ChS119							0.08
ZnSt					0.08	0.08	0.08
ZnOct			0.08				
MgNaph	0.08			0.08			
MnOct		0.08					
Evaluation based on observations							
At room temp. after preparation	Thin liquid	Solid after mixing.	Thin liquid	Solid after mixing.	Thin liquid	Thin liquid	Thin liquid
At 100 °C after heating	Solid after 25 min.	Solid	Solid after 6 min.	Solid after 3 min.	Solid after 8 min.	Solid after 5min.	Solid after 10 min.
At room temp. after cooling	Solid	Solid	Solid	Solid	Solid	Solid	Solid
At 135 °C after heating	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid	Thin liquid

At room temp. after cooling	Solid	Solid	Solid	Solid	Solid	Solid	Solid

The results clearly show that the combination of catalysts is an effective way to accelerate the urethane formation. It is especially notable that the combination of hindered amine stabilizers and zinc stearate lubricants (both well known additives used in polyolefin processing) yields an effective catalyst/co-catalyst system.

Example 2.

Optimization of grafting/crosslinking conditions in a paraffin model system.
Crosslinking by grafted aliphatic alcohol and polyphenol-diisocyanate preopolymer

Preliminary optimization of crosslinking/grafting conditions was performed in a model system, wherein the polyethylene matrix was replaced by a liquid paraffin (hereinafter abbreviated as PARF, mixture of saturated hydrocarbons, carbon number n<15, Boiling point < 350 °C). This low molecular matrix made possible an easy screening of the crosslinking efficiency (liquid/gel) in a dilute non-polar medium.

In this experiment cross-linkage was built up by grafting an unsaturated compound, containing an aliphatic alcohol function (hydroxyethyl methacrylate, HEMA), on the saturated paraffin backbone according to the following reaction

$$C_nH_{2n+2} + CH_2=C(CH_3)-COO-CH_2-CH_2-OH + Perox \rightarrow PARF-OH$$

and by reacting the grafted alcohol with an aromatic polyol - aromatic diisocyanate prepolymer, which can be regarded as a phenol blocked polyisocyanate:

$$...OOC-NH-Ph^1-NH-COO-Ph^2-OOC-NH-Ph^1-NH-COO...$$

where Ph^1 is an aromatic group belonging to the diisocyanate and Ph^2 is another aromatic group belonging to the (phenolic) polyol. (The reagents were chosen so that Ph^1 is substituted with 2 isocyanates and Ph^2 is substituted with 3 phenolic groups, and the molar ratio of Ph^1 and Ph^2 is chosen so that the concentrations of the isocyanate and

5 phenolic groups are equal). The crosslinks are formed according to the following schematic reaction

2PARF-OH   +   ...OOC-NH-Ph^1-NH-COO-Ph^2-OOC-NH-Ph^1-NH-COO...→

10 **PARF-O-CO-NH-Ph^1-NH-COO- Ph^2-OOC-NH-Ph^1-NH-CO-O-PARF**
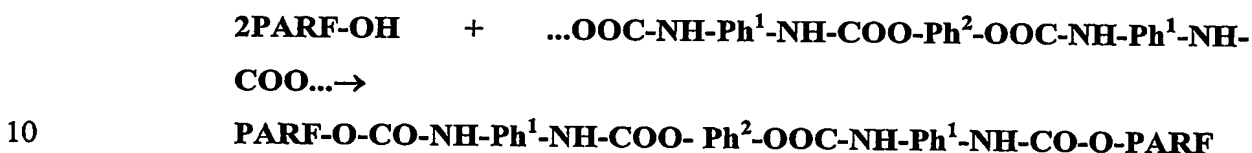
where the thermally reversible urethane bonds are those located between the Ph^1 and Ph^2 groups and a part of the phenolic OH substituents on Ph^2 are released in the reaction. These bonds can dissociate thermally at temperatures (around 130 °C), where

15 the other urethane bond between the grafted paraffin /PARF-OH/ and the other aromatic isocyanate group remains intact. Rheological measurement (Höppler-viscosimeter) was applied for the detection the degree of crosslinking.

As radical source Luperox F90P (1,3 1,4-bis(terc-butylperoxyisopropyl)benzene,

20 powder on silica surface, conc. 90%, commercially available products of Atofina, France, the active agent hereinafter abbreviated as Perox TB) was used. In preliminary experiments 0.5, 1.0, 2.0, 4.0 and 8.0 phr Perox TB was added to 20 cm^3 paraffin and heat-treated at 130 °C for 10 minutes. It turned out that below 2.0 phr peroxide addition the viscosity decreases rather than increases, which indicates that chain scission is more

25 effective than crosslinking. In the 2.0-8.0 phr peroxide range the viscosity increases gradually (by about 50%). To compensate for the chain scission in a next series of experiments the same amounts of peroxide were added to the paraffin but in combination with 2/3 mol triallyl-iscyanurate (a well known trifunctional crosslinking co-agent, commercial product of Degussa AG Germany, hereinafter abbreviated as

30 TAIC, 2/3 mol to each mol of Perox TB) and the crosslinking experiment was repeated. In this case the viscosity increased in the whole concentration range, for e.g. 4 phr Perox TB +TAIC the viscosity tripled in comparison to the non-crosslinked system. The

Arrhenius plot (log η − 1/T) of the paraffin crosslinked with 4 phr Perox TB and TAIC is shown in Fig. 1. The slope of the curve (proportional to the activation energy of the viscous flow) is fairly constant in the whole temperature range studied, indicating no major change in the mechanism of flow. The system crosslinked with 8 phr Perox TB and TAIC was a gel, so the viscosity could not be measured.

Now we could start to optimise the grafting/crosslinking conditions on the paraffin model using the chemicals shown in Table 5.

Table 5. List of the chemicals used to model a reversibly crosslinked system.

Component	Role of component	Characteristics
Paraffin oil (PARF)	Matrix	C_nH_{2n+2} n < 15 Bp < 350°C
Luperox F90P (Perox TB) Atofina	Radical initiator Derivative of terc. butyl peroxide	Powder on Silica surface Conc: 90 %
Triallyl-isocyanurate (TAIC), Degussa AG	trifunctional crosslinking co-agent	Crystalline solid
Phloroglucinol (1,3,5-trihydroxy-benzene) (PHL)	Aromatic polyol	Crystalline solid
2-Hydroxyethyl-methacrylate (HEMA), Aldrich	aliphatic alcohol grafted onto PARF to fix the isocyanate	Liquid
Zn Stearate (ZnSt)	Urethane formation catalyst	See Table 2.
Chimassorb 944 (ChS944)	Urethane formation catalyst	See Table 2.

Toluylene-di-isocyanate (TDI)		See Table 1.
Bentone SB (RHEOX Inc)	Dispersing agent	Organophilic montmorillonite

From these HEMA was used to anchor the reversible crosslink site (made of PHL and TDI), Perox TB was used to graft HEMA, ZnSt and ChS944 were the urethane formation catalysts (see Example 1) while Benotne SB played a special role (processing aid). Initial experiments showed that miscibility problems may arise among the various components, which can be largely removed if the various components are absorbed by a small amount of organophilic montmorillonite.

The samples described in Table 6. were prepared according to the following, two-step method: first one phr Bentone was loaded in the test tube, then Peroxide TB and HEMA were weighed to Bentone. The components were intensively homogenised and then gradually diluted with 20 cm³ PARF oil during intensive homogenization. Grafting was performed at 130°C, in 10 min, without mixing. In a second test-tube one phr Bentone was loaded, then TDI, PHL and the catalysts were loaded, intensively homogenised, and then diluted with the above prepared, grafted and cooled, PARF oil applying intensive homogenisation. The urethane formation was performed by heat treatment at 130°C, in 10 min, without mixing.

Table 6. Samples prepared for optimizing thermo-reversible crosslinking

	Relative amounts of components				
Perox-TB (to 100 wt PARFF)	0,5 phr	1,0 phr	2,0 phr	4,0 phr	8,0 phr
PARF	20 cm³ (100 wt)				
TAIC	2 Mol to 3 Mol Perox-TB				
HEMA	2 Mol to 1 Mol Perox-TB				
TDI	2 Mol to 1 Mol Perox-TB				

PHL	2 Mol to 3 Mol TDI
ZnSt	6 wt to 100 wt TDI
ChS944	6wt to 100 wt TDI
Bentone	2 phr (to 100 wt PARF)

The breakage of the thermo-reversible urethane bonds was detected indirectly, by monitoring the changes in sample viscosity on heating and cooling. Structural changes were indicated by a relatively sudden change in the activation energy of viscous flow. Fig.2. shows the Arrhenius plot of viscosity for the sample prepared with 0.5 phr Perox TB and other additives, while Fig. 3. shows similar results for the sample prepared with 2 phr Perox TB. Obviously, the 0.5 phr sample does not show any sign of alteration in the flow mechanism (and activation energy), while the 2 phr sample exhibits sudden changes in the activation energy of viscous flow both on heating and on cooling – indicative of the thermo-reversible crosslinking.

Examples 3-5

LDPE based compounds with thermally reversible urethane crosslinks. Crosslinking by grafted aliphatic alcohol and polyphenol-TDI prepolymer

Compounds according to the invention were prepared by a two-step grafting/crosslinking procedure. The materials used are described in Table 7, the compositions are listed in Table 8.

Table 7. Materials used for preparing examples 3-5.

Component	Role of component	Characteristics
Tipolen FB 243-51 (TVK Rt., Hungary)	Matrix	LDPE Mp.111 °C Density. 0,924 g/cm3 MFI: : 0,8 (190°C/2,16 kg) (g/10 min)
Luperox F90P (Perox TB: 1,3-1,4-bis(tert-butylperoxyisopropyl)-benzene on silica powder) (ATOFINA, France)	Radical initiator

Derivative of terc. Butyl peroxide | See Table 5. |
| **2-Hydroxyethyl-methacrylate (HEMA),** | Aliphatic alcohol with | See Table 5. |

Aldrich	unsaturation	
Phloroglucinol (PHL)	Aromatic polyol	See Table 5.
Toluylene-2,4-diisocyanate (TDI) (Aldrich)	Aromatic di-isocyanate	See Table 1.
CHIMASORB 944 (ChS944) (CIBA-GEIGY)	Urethane formation catalyst	See Table 2.
Zinc-stearate (ZnSt)	Urethane formation catalyst	See Table 2.
Bentone SB (RHEOX Inc.)	Dispersing agent	See Table 5.

Table 8. The composition of compounds (examples 3-5).

		Example 3		Example 4		Example 5	
sample code		02-35a		02-36a		02-37a	
Component	ratio	**mol**	**g**	**mol**	**g**	**mol**	**g**
Tipolen FB 243-51 (matrix)			230		230		230
	First additive package						
Perox-TB[*]	0.5-1.5 phr	0.0034	1.15	0.0068	2.3	0.0102	3.45
2-Hydroxy-ethyl- methacrylate (HEMA)	2 mol HEMA / 1 mol Perox-TB	0.0068	0.88	0.0136	1.77	0.0204	2.65
Bentone	1 phr		2.3		2.3		2.3
	Second additive package						
Toluylene-2,4-diisocyanate (TDI)	2 mol TDI /1 mol Perox-TB	0.0068	1.18	0.0136	2.37	0.0204	3.55
Phloroglucinol (PHL)	2 mol PHL / 3 mol TDI	0.0045	0.57	0.0091	1.14	0.0136	1.71
Zinc-stearate (ZnSt)	6% to TDI		0.07		0.14		0.21
Chimasorb 944 (ChS944)	6% to TDI		0.07		0.14		0.21
Bentone	1 phr		2.3		2.3		2.3

[*]Perox TB is given as active ingredient content (90% of the total weight)

5

The ingredients of the samples were homogenized in a Brabender PL 2000 type laboratory internal-mixer (kneader), equipped with a chamber of 250 cm^3 useful capacity. The mixing parameters are listed in Table 9.:

5   Table 9. Processing parameters in the Brabender kneader

Rotation of screws	50 rpm
Starting temperature	130 °C
Mixing time	40 min

The temperature profile in the course of the mixing process was as follows in Table 10.:

10   Table 10. Temperature program of the two-step process in the Brabender kneader

Period	Temperature (°C)
Start of the mixing	130
First feed	135
Second feed	140
End of the mixing	145

The appropriate amount of LDPE was fed into the chamber, and the polymer was melted. In the first step the mixture of Bentone-Perox TB-HEMA (first additive
15   package) was added to the polymer. The first additive package was prepared by loading first the Bentone into a glass beaker, followed by the peroxide and finally by the liquid HEMA. The components were intensively homogenized by a glass rod, until a highly viscous paste was obtained. This paste was gradually added to the melted LDPE during a continuous mixing at 135 °C. The grafting was performed in 10 min also during
20   continuous mixing process. In the second step the mixture of Bentone-TDI (or MDI)-PHL-catalysts (second additive package) was added to the polymer. The second additive package was prepared similarly as the first one, that is, in another beaker glass first the Bentone was loaded, then the PHL, the catalysts (ZnSt, ChS944) and finally the liquid isocyanate component (TDI). The components were intensively homogenized by

a glass rod until a paste was obtained, and then the paste was added to the above grafted LDPE, applying 10 min further homogenization in the Brabender mixer at 145°C. The formation of urethane linkages with the HEMA hydroxyl takes place already at this temperature, while the urethane formation of aromatic hydroxyl and isocyanate takes

5   place only below 130°C.

Examples 6-8

LDPE based compounds with thermally reversible urethane crosslinks. Crosslinking by

10   *grafted aliphatic alcohol and polyphenol-MDI prepolymer*

Compounds according to the invention were prepared by an identical two-step grafting/crosslinking procedure as described for examples 3-5, but, instead of TDI (toluylene 2,4- diisocyanate) MDI (methylene-diphenyl-diisocyanate, ONGRONAT

15   HS-44, a commercial product of BorsodChem Rt., Hungary) was used as isocyanate component. The compositions are listed in Table 11.

Table 11. The composition of compounds (examples 6-8).

		Example 6		Example 7		Example 8	
sample code		02-44		02-45		02-46	
Component	ratio	mol	g	mol	g	mol	g
Tipolen FB 243-51 (matrix)			230		230		230
	First additive package						
Perox-TB*	0.5-1.5 phr	0.0034	1.15	0.0068	2.3	0.0102	3.45
2-Hydroxy-ethyl-methacrylate (HEMA)	2 mol HEMA / 1 mol Perox-TB	0.0068	0.88	0.0136	1.77	0.0204	2.65
Bentone	1 phr		2.3		2.3		2.3
	Second additive package						
Methylene-diphenyl diisocyanate (MDI)	2 mol TDI /1 mol Perox-TB	0.0068	1.70	0.0136	3.40	0.0204	5.10

SUBSTITUTE SHEET (RULE 26)

Phloroglucinol (PHL)	2 mol PHL / 3 mol MDI	0.0045	0.57	0.0091	1.14	0.0136	1.71
Zinc-stearate (ZnSt)	4% to MDI		0.10		0.20		0.31
Chimasorb 944 (ChS944)	4% to MDI		0.10		0.20		0.31
Bentone	1 phr		2.3		2.3		2.3

*Perox TB is given as active ingredient content (90% of the total weight)

Examples 9-11

5   *LDPE based compounds with thermally reversible urethane crosslinks. Crosslinking by grafted phenol and grafted isocyanate*

Compounds according to the invention were prepared by a two-step grafting/crosslinking procedure, similar to those described for examples 3-5 (processing
10 parameters are identical with those described in Tables 9 and 10), but the materials and the additive packages were different. Materials used are described in Table 12, sample compositions in Table 13.

Table 12. Materials used in the synthesis of examples 9-11.

Component	Role of component	Characteristics
Tipolen FB 243-51 (TVK Rt. Hungary)	Matrix	LDPE Mp.111 °C Density. 0,924 g/cm3 MFI: : 0,8 (190°C/2,16 kg) (g/10 min)
Luperox F90P (Perox TB: 1,3-1,4-bis(tert-butylperoxyisopropyl)-benzene on silica powder) (ATOFINA, France)	Radical initiator Derivative of terc. Butyl peroxide	See Table 5.
2-Hydroxyethyl-	Aliphatic alcohol	See Table 5.

methacrylate (HEMA)	with unsaturation	
2-Allylphenol (APh) (Merck)	Aromatic alcohol with unsaturation	Liquid, Mw: 134,18 g/mol mp.-7- -5 °C bp.219-221 °C
2-Isocyanato-ethyl-methacrylate (IEM)	Aliphatic isocyanate with unsaturation	Liquid, Mw: 155.16 g/mol m.p. –45 °C, bp. 211 °C
CHIMASORB 944 (ChS944) (CIBA-GEIGY)	Urethane formation catalyst	See Table 2.
Zinc-stearate (ZnSt)	Urethane formation catalyst	See Table 2.
Bentone SB (RHEOX Inc.)	Dispersing agent	See Table 5.

Table 13. The composition of compounds (examples 9-11).

		Example 9		Example 10		Example 11	
sample code		02-50		02-51		02-52	
Component	ratio	**mol**	**g**	**mol**	**g**	**mol**	**g**
Tipolen FB 243-51 (matrix)			230		230		230
	First additive package						
Perox-TB[*]	0.5-1.5 phr	0.0017	0.58	0.0034	1.15	0.051	1.73
2-Allylphenol (APh)	2 mol APh / 1 mol Perox-TB	0.0034	0.46	0.0068	0.92	0.0102	1.37
Bentone	1 phr		2.3		2.3		2.3
	Second additive package						

Perox-TB[*]	0.5-1.5 phr	0.0017	0.58	0.0034	1.15	0.051	1.73
2-Isocyanato-ethyl-methacrylate (IEM)	2 mol IEM /1 mol Perox-TB	0.0034	0.52	0.0068	1.04	0.0102	1.58
Zinc-stearate (ZnSt)	13% to IEM		0.07		0.14		0.21
Chimasorb 944 (ChS944)	13% to IEM		0.07		0.14		0.21
Bentone	1 phr		2.3		2.3		2.3

[*]Perox TB is given as active ingredient content (90% of the total weight)

The appropriate amount of LDPE was fed into the chamber, and the polymer was melted. In the first step the first additive package of Bentone-Perox TB-allylphenol
5   (APh) was added to the polymer. The additive package was prepared by loading first the Bentone in a glass beaker, then the peroxide and finally the liquid APh. The components were intensively homogenized by a glass rod until a strong viscous paste was obtained. The paste was gradually added to the melted LDPE during continuous mixing at 135 °C. Grafting reaction was finished in 10 min also during continuous
10   mixing. In the second step the additive package of Bentone - isocyanato-ethyl-methacrylate (IEM) - catalysts was added to the polymer. This package was prepared similarly to the first one, that is, in another glass beaker first the Bentone was loaded, then Perox TB, the catalysts (ZnSt, ChS944) and finally the liquid isocyanate components (IEM). The components were intensively homogenized by a glass rod until
15   the formation of a paste, and then the paste was added to the above grafted LDPE, applying 10 min further homogenisation in the Brabender mixer at 145°C.

Evaluation of the compounds prepared under Examples 3-11

20   Figures 4, 5 and 6. show the micro-thermal analysis curves of the compounds prepared under examples 3-5, 6-8 and 9-11 respectively. For comparison the μTA curve a non-crosslinked PE sample is also shown in each figure. Up to the melting point the thermal expansion is detected by a positive movement. In the melting-range (112-116 °C for the non-crosslinked samples) the sample softens and the probe penetrates the sample
25   surface. The melting point can be estimated by the intersection of the slopes. In the case of the samples containing the reversible crosslinks the melting transition also appears as a change in the slope but, due to the presence of crosslinks the molten polymer does not

flow, the elastomeric network still exerts some resistance to the penetration. When the urethane linkages begin to dissociate (in the 130-145 °C range) the slope increases further and the samples soften, similarly to the non-crosslinked samples. There is one exception: curve 02-46, corresponding to the sample prepared with 2 phr peroxide and

5   MDI-based polyphenol – isocyanate prepolymer, where there is no softening upon further heating. It seems that in this case 2 phr peroxide already caused a true crosslinking of the LDPE sample, i.e. irreversible C-C crosslinks are also formed in addition to the thermally reversible urethane linkages. It also shows that the selection of proper additive packages is a delicate task. Anyway, all three types of compounds

10   prepared with 1 phr peroxide and corresponding other additives seems to be acceptable.

The actual recyclability of three compounds prepared according to the invention (according to examples 4, 7 and 10, all with 1 phr peroxide and the corresponding additives) was checked by measuring the torque in a kneading chamber of the

15   Brabender Plastograph at various temperatures (110 and 140 °C) and compared to non-crosslinked LDPE. The results are summarized in Table 14.

Table 14   Processing characteristics of PE and compounds prepared with various crosslinking additives

Cycle of processing	Characteristics	PE		Example 4		Example 7		Example 10	
Processing temperature, °C		110	140	110	135	110	140	110	140
First cycle	Melting	Yes	Yes	No	Yes	No	Yes	No	Yes
	Start of melting, min	3	1.5	-	7	-	3.5	-	2.5
	Torque, Nm	50*	60**	-	75	.	77	-	80
Second cycle	Melting							No	Yes
	Start of melting, min							-	3
	Torque, Nm							-	70

*   PE compound prepared by use of 2 phr Bentone

** Virgin PE

5 As shown by the data, at 110 °C only the non-crosslinked sample can be melt-processed, the others, having thermally reversible crosslinks can only be processed at a higher temperature, exceeding the dissociation temperature of the urethane bond. The presence of crosslinks is also shown by the fact that the non-crosslinked LDPE sample melts at 140 °C within 1.5 min, while the crosslinked samples within 2.5-7 min. In the case of Example 10 a repeated processing cycle was also performed to prove the

10 repeated processability of the polymer compound according to the invention.